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THE CRYSTAL STRUCTURE OF SODIUM METABORATE, $\text{Na}_3(\text{B}_3\text{O}_6)$

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
1938

By
SSU-MIEN FANG

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The Crystal Structure
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With 4 figures

The Crystal Structure of Sodium Metaborate $Na_3(B_3O_6)$.

By Ssu-Mien Fang, Chicago (USA.).

Cole, Scholes and Amberg¹⁾ described crystals of sodium metaborate. The symmetry was reported as hexagonal, which agrees with early observations (Groth, Wunder, Van Klooster etc.). The crystals were found to be optically uniaxial with strong birefringence.

The specific gravity of the crystal was given as 2.343 and the dimensions of the hexagonal cell were given as

$$a_0 = 6.85 \text{ \AA} \text{ and } c_0 = 10.95 \text{ \AA}.$$

On the basis of their reported density and cell dimensions we calculate 9.6 molecules of $NaBO_2$ per unit cell, while Cole, Scholes, and Amberg claimed 16 molecules of $Na_2O \cdot B_2O_3$. Their various statements concerning the lattice structure are thus in conflict with each other.

Crystals of $NaBO_2$ were prepared by fusing Na_2CO_3 with B_2O_3 in proper proportions and allowing it to cool rapidly. Hexagonal needle-shaped crystals were found in the cavity inside the solid cake. Perfect single crystals were picked out by means of a microscope.

We determined the specific gravity of the crystal by the suspension method and found it to be $2.464 \pm .005$. The value reported by Cole, Scholes, and Amberg is thus about 5 per cent too low.

The crystals were examined by the Laue method and the rotating crystal method. Oscillation photographs were taken with copper K -radiations filtered through a thin nickel foil. The hexagonal X - and Z -axes served as rotating axes.

We found the dimensions of the hexagonal cell to be

$$a = 11.91 \pm .02 \text{ \AA}, \quad c = 6.45 \pm .01 \text{ \AA}$$

with 18 (18.006) molecules in the cell. The cell dimensions given by Cole, Scholes, and Amberg do not show any relationship to those found by us. They obtained their results from powder crystal photographs. An inspection of their data shows, however, that the interpretation is entirely incorrect and should not be further considered²⁾.

1) Cole, S. S., Scholes, S. R., and Amberg, C. R., System $B_2O - B_2O_3$: II. Properties of Anhydrous and Hydrated Metaborates of Sodium and Potassium. J. Amer. Ceram. Soc. 18 (1935) 58.

2) Our preliminary results for cell size and space group were published in a short note in the J. Amer. Ceram. Soc. 20 (1937) 215. The manuscript of

No reflections were observed from planes for which $h + 2k + l = 3n$, so the true unit cell is rhombohedral with

$$R = 7.22 \pm .01 \text{ \AA} \text{ and } \alpha = 111^\circ 29'$$

and with 6 molecules of NaBO_2 per unit cell.

Laue as well as oscillation photographs showed the symmetry characteristic of the point group $3m(D_{3d})$. No reflections were observed from planes (p, p, r) when r is odd, (p, q, r) being Miller indices referred to the rhombohedral cell. This fact indicates that the space group must be either $D_{3d}^6 - R\bar{3}c$ or $C_{3v}^6 - R3c$.

Parameter values were found first by the Patterson method of Fourier analysis and then by the ordinary Fourier analysis: By the Patterson method the structure was depicted on a projection plane normal to the three-fold axis of symmetry. The outstanding peaks must be attributed to the sodium positions. Although there were small peaks on the bisectrices the boron and oxygen positions could not be accurately measured, but the analysis proved $D_{3d}^6 - R\bar{3}c$ to be the correct space group. To obtain the accurate positions for boron and oxygen atoms and ordinary Fourier analysis was next made with the estimated structure factor values and was plotted on the projection plane normal to the three-fold axis as shown in Fig. 1. The parameters so obtained are

Atoms	$2\pi(u - \frac{1}{4})$	$2\pi u$	u
Na	160.5 ± 1	250.5 ± 1	$.696 \pm .003$
B	40 ± 2	130 ± 2	$.362 \pm .006$
O _I	82.5 ± 2	172.5 ± 2	$.479 \pm .006$
O _{II}	-40 ± 2	50 ± 2	$.138 \pm .006$

The expression for the structure factor is

$$F_{p,q,r} = 2 \sum_i f_i \{ \cos 2\pi [p x_i + q y_i + r z_i] \\ + \cos 2\pi [p y_i + q z_i + r x_i] \\ + \cos 2\pi [p z_i + q x_i + r y_i] \},$$

where

$$(x, y, z) \equiv (u, \frac{1}{2} - u, \frac{1}{4}).$$

Since

$$p + q + r = l,$$

this note was submitted to Cole, Scholes, and Amberg, who in a succeeding note reported $2.462 \pm .002$ as the redetermined value of the density. Their attempt to interpret the powder photographs according to the cell dimensions reported by us is unsatisfactory, as only a small fraction of the diffraction lines are correctly indexed. — (Note added in proof.)

we have

$$F_{p,q,r} = 2 \sum_i f_i \left\{ \cos 2\pi \left[(p-q) \left(u_i - \frac{1}{4} \right) + \frac{1}{4} l \right] \right. \\ \left. + \cos 2\pi \left[(q-r) \left(u_i - \frac{1}{4} \right) + \frac{1}{4} l \right] \right. \\ \left. + \cos 2\pi \left[(r-p) \left(u_i - \frac{1}{4} \right) + \frac{1}{4} l \right] \right\}.$$

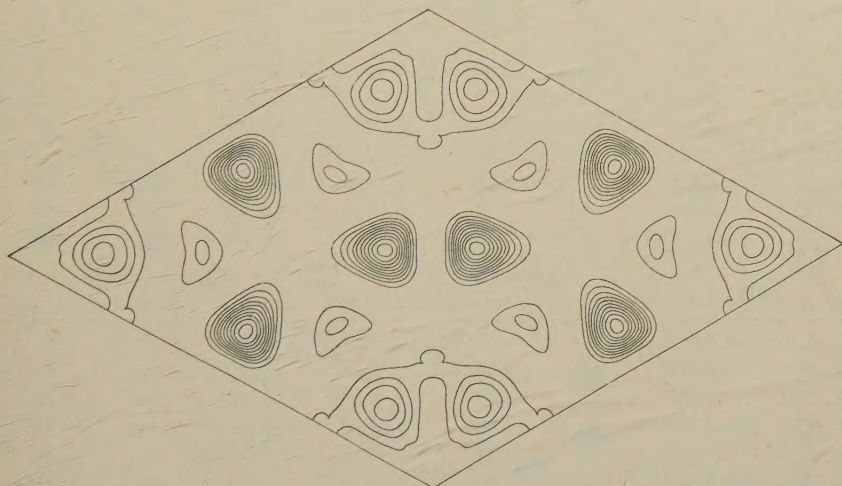


Fig. 1. This diagram shows the electron density projected on the (111)-plane. The outstanding peaks are sodium atoms and the rest are oxygen and boron atoms.

Here the f values were taken after the data of R. W. James and G. W. Brindley¹⁾. The structure factors were calculated and are given in the following tables:

a) For $p + q + r = l = 0$.

p, q, r	$\sin \theta/\lambda$	obs. I	cal. F	p, q, r	$\sin \theta/\lambda$	obs. I	cal. F
1, 0, $\bar{1}$	.0842	vw	5	6, $\bar{2}$, $\bar{4}$	.4468	nil	.2
2, $\bar{1}$, $\bar{1}$	.1461	vw	11	6, $\bar{1}$, $\bar{5}$	.4700	nil	7
2, 0, $\bar{2}$	.1685	vw	8	6, 0, $\bar{6}$	.5063	m	29
3, $\bar{2}$, $\bar{1}$	.2230	wm	10	7, $\bar{3}$, $\bar{4}$	.5137	vw	1
3, 0, $\bar{3}$	.2529	vs	54	7, $\bar{2}$, $\bar{5}$	.5268	nil	3
4, $\bar{2}$, $\bar{2}$	.2922	vw	1	7, $\bar{1}$, $\bar{6}$	.5538	nil	3
4, $\bar{1}$, $\bar{3}$	.3040	wm	6	8, $\bar{4}$, $\bar{4}$	.5850	vw	2
4, 0, $\bar{4}$	.3376	vw	2	7, 0, $\bar{7}$	.5910	w	1
5, $\bar{2}$, $\bar{3}$	.3683	w	3	8, $\bar{3}$, $\bar{5}$	.5910	vw	9
5, $\bar{1}$, $\bar{4}$	.3870	nil	.3	8, $\bar{2}$, $\bar{6}$	.6082	vw	8
5, 0, $\bar{5}$	.4220	vw	12	8, $\bar{1}$, $\bar{7}$	.6470	nil	1
6, $\bar{3}$, $\bar{3}$	.4385	s	69				

1) James, R. W., and Brindley, G. W., *Philos. Mag.* **12** (1934) 404.

b) For $p + q + r = l = 1$.

p, q, r	$\sin \theta/\lambda$	obs. I	cal. F	p, q, r	$\sin \theta/\lambda$	obs. I	cal. F
1, 0, 0	.0487	nil	0	1, 4, $\bar{4}$	.3410	s	29
1, 1, $\bar{1}$	.0975	nil	0	5, $\bar{2}$, $\bar{2}$	.3412	nil	0
2, $\bar{1}$, 0	.1295	vw	2	5, 3, $\bar{1}$	.3517	vw	3
1, 2, $\bar{2}$	.1755	vs	36	5, $\bar{4}$, 0	.3809	nil	1
3, $\bar{1}$, $\bar{1}$	.1948	nil	0	3, 3, $\bar{5}$	.3900	nil	0
3, $\bar{2}$, 0	.2121	vs	40	2, 4, $\bar{5}$	.3990	vw	4
2, 2, 3	.2440	vs	0	6, 3, $\bar{2}$	.4167	vw	3
1, 3, $\bar{3}$	.2580	nil	29	1, 5, $\bar{5}$	.4250	s	23
4, $\bar{2}$, $\bar{1}$	.2714	vs	35	6, $\bar{4}$, $\bar{1}$	.4332	vw	1
4, $\bar{3}$, 0	.2962	s	26	3, 4, $\bar{6}$	.4650	xw	3
2, 3, $\bar{4}$	.3190	vw	2	6, $\bar{5}$, 0	.4650	m	18

c) For $p + q + r = l = 2$.

p, q, r	$\sin \theta/\lambda$	obs. I	cal. F	p, q, r	$\sin \theta/\lambda$	obs. I	cal. F
1, 1, 0	.0487	xs	61	5, $\bar{3}$, 0	.3410	w	18
2, 0, 0	.0975	xs	65	3, 3, $\bar{4}$	.3412	vs	40
1, 2, $\bar{1}$	.1295	vs	21	2, 4, $\bar{4}$	.3517	vw	10
3, $\bar{1}$, 0	.1755	vs	26	1, 5, $\bar{4}$	.3809	wm	21
2, 2, $\bar{2}$	.1948	vs	34	6, $\bar{2}$, $\bar{2}$	.3900	m	27
1, 3, $\bar{2}$	.2121	ms	21	6, 3, $\bar{1}$	.3990	s	34
4, $\bar{1}$, $\bar{1}$	.2440	vs	28	3, 4, $\bar{5}$	.4167	m	22
4, $\bar{2}$, 0	.2580	s	16	6, $\bar{4}$, 0	.4250	m	19
2, 3, $\bar{3}$	.2714	ms	26	2, 5, $\bar{5}$	.4332	vw	11
1, 4, $\bar{3}$	.2962	vw	12	1, 6, $\bar{5}$	.4650	w	11
5, $\bar{2}$, $\bar{1}$	.3190	w	13	7, $\bar{3}$, $\bar{2}$	.4650	w	16

Fig. 2 shows a projection of the structure on a plane normal to the three-fold axis. The atoms lying in layers normal to the three-fold axis 3.23 Å apart. All atoms lie on two-fold rotation axis.

The boron atoms are linked to the oxygen atoms to form ring-shaped radicals $(B_3O_6)^{-3}$. The ring is rather of three BO_3 triangles (see Fig. 3) which are almost equilateral and share corners with each other. The oxygen atoms consist of two types. We call the shared oxygen atoms O_I and the unshared ones O_{II} . The $O_{II}-O_{II}$ distance is 2.32 Å and the O_I-O_{II} distance 2.37 Å. The average distance for $O-O$ is 2.35 Å which agrees with those given by Zachariasen from his work on CaB_2O_4 ¹) in 1931 and his recent work on potassium metaborate, $K_3(B_3O_6)^2$).

1) Zachariasen, W. H., and Ziegler, G. E., The Crystal Structure of Calcium Metaborate, *CaB_2O_4*, Z. Kristallogr. **83** (1932) 354. Also, Zachariasen, W. H., The Crystal Lattice of Calcium Metaborate, *CaB_2O_4*, Nat. Acad. Sci. **17** (1934) 617.

2) Zachariasen, W. H., The Crystal Structure of Potassium Metaborate, $K_3(B_3O_6)$. J. chem. Physics **5** (1937) 949.

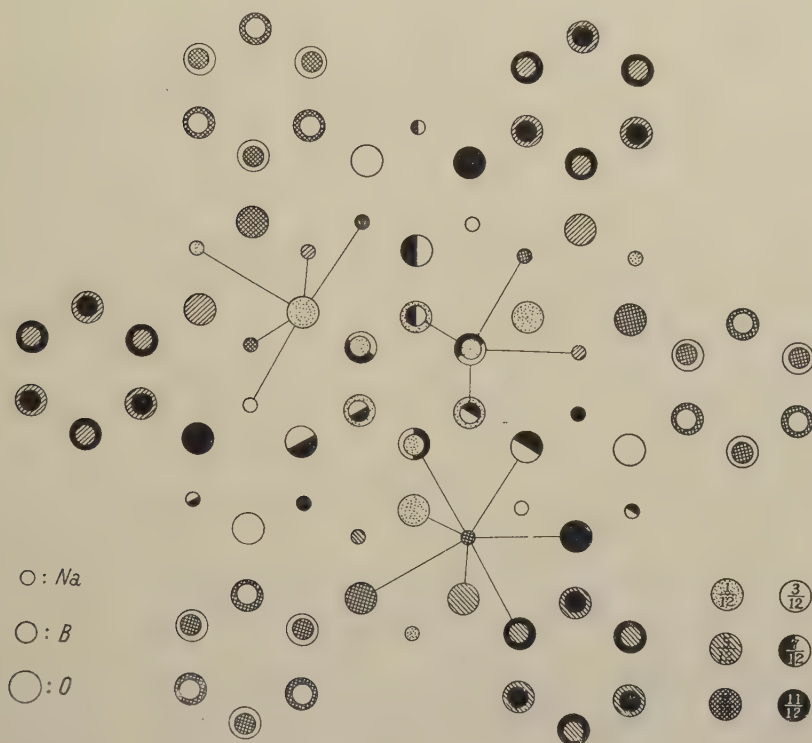


Fig. 2. This diagram shows the structure projected on the c -face. The heights of the atoms are given in fractions of the periodicity along the three-fold axis (i. e. 6.46 Å).

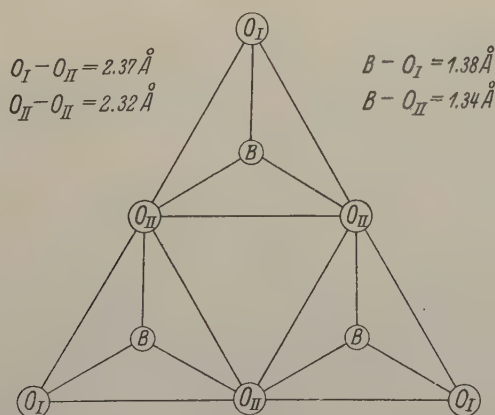


Fig. 3. This figure shows the ring-shaped B_3O_6 radical formed of three BO_3 triangles, which share corners. The interatomic distances are given in the figure.

The $B-O_I$ and $B-O_{II}$ distances were measured to be 1.38 Å and 1.34 Å respectively, whereas Zachariasen found 1.34 Å for $B-O_I$ and 1.38 Å for $B-O_{II}$ in the structure of $K_3(B_3O_6)$. The boron atoms are apparently distorted in opposite directions in these two cases. This discrepancy arises from the fact that the B and O_{II} positions in the diagram of the structure of the crystal, $Na_3(B_3O_6)$, are too close to be separated and accurately measured. However, the average $B-O$ distance, 1.36 Å, is in good agreement with that given by Zachariasen on the structure of $K_3(B_3O_6)$.

Each sodium atom is surrounded by seven oxygen atoms (Fig. 2) — one O_I at 2.58 Å, two O_I at 2.51 Å, two O_I at 2.52 Å, and two O_{II} at 2.53 Å. Hereby we find the average $Na-O$ distance equal to 2.53 Å,

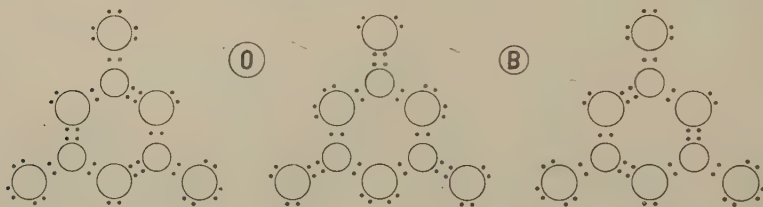


Fig. 4. This diagram shows the three possible electronic structures for the B_3O_6 radical with the concept of covalent bonds.

which agrees very closely with the value 2.49 Å for the sum of radii of Na^+ and O^{-2} for a coordination number 7 according to Zachariasen's formula¹).

Every O_I atom is linked to one boron atom at 1.38 Å and five sodium atoms — one at 2.58 Å, two at 2.52 Å, and two at 2.51 Å. Whereas an oxygen atom of the second type is linked to two boron atoms at 1.38 Å and two sodium atoms at 2.53 Å.

To explain the radical B_3O_6 with the concept of covalent bonds we may assume it with three forms of electronic structure as shown in Fig. 4.

We cannot claim to have determined the positions of boron and oxygen atoms with sufficient accuracy to be able to decide which of the three possibilities is the more important. Our result may only be taken to indicate that there is considerable resonance between the three structures.

1) Zachariasen, W. H., A Set of Empirical Radii for Ions with Inert Gas Configuration. *Z. Kristallogr.* 80 (1931) 137.

The O_{II} atoms are shared between two boron and two sodium atoms and have a bond strength of 2.29, while the O_I atoms are shared between one boron and five sodium atoms and have a bond strength of 1.71.

It is very interesting to point out that sodium metaborate, $Na_3(B_3O_6)$ has the same structure as the potassium compound but with somewhat different parameter values. Usually sodium has a coordination number of six with respect to oxygen, while potassium is generally linked to 8—10 oxygens. Oxygen compounds of sodium and potassium therefore as a rule have different crystal structures (for example $NaNO_3-KNO_3$, $NaClO_3-KClO_3$, $Na_2SO_4-K_2SO_4$, $NaClO_4-KClO_4$), so that the isomorphism between sodium and potassium metaborates represent a rare case.

Ghosh and Das¹⁾ observed the Raman shifts of BO_2 and concluded that it is a triatomic ion with non-linear and symmetric structure. Nielsen and Ward²⁾ repeated the observation on sodium metaborate and drew the different conclusion that it is a triatomic ion but linear in structure.

Neither the result of Ghosh and Das nor that of Nielsen and Ward is compatible with crystal structure investigations. In crystals boron is found to be surrounded either by three or by four oxygen atoms, and this must be true also in the liquid or glassy states.

Summary.

The unit cell of sodium metaborate is rhombohedral with $R = 7.22 \pm .01 \text{ \AA}$ and $\alpha = 111^\circ 29'$, the density is $2.464 \pm .005 \text{ gm/cm}^3$, and there are six molecules of $NaBO_2$ per unit cell. The space group is $D_{3d}^6-R\bar{3}c$. The atomic positions are $(u, \frac{1}{2}-u, \frac{1}{4})\bar{C}$. For the parameter values we found $.696 \pm .003$ for Na , $.362 \pm .006$ for B , $.479 \pm .006$ for O_I , and $.438 \pm .006$ for O_{II} . All atoms are found lying in layers normal to the three-fold axis $3.23 \text{ \AA}$ apart. The boron and oxygen atoms are linked together to form ring-shaped radicals, $(B_3O_6)^{-3}$, consisting of three BO_3

1) Ghosh, J. C., and Das, S. K., Raman Effects in Inorganic Compounds. J. phys. Chem. **36** (1932) 586.

2) Nielsen, J. Rud., and Ward, N. E., Raman Spectrum and Structure of the Metaborate Ion. J. chem. Physics **5** (1937) 201.

In a paper presented at the meeting of Amer. Phys. Soc. at Indianapolis on Dec. 30, 1937, Nielsen, Ward, and Dodson reported the presence of additional frequencies in the Raman spectra of sodium metaborate. Their previous conclusion that the metaborate group is similar to CO_2 was therefore withdrawn. — (Note added in proof.)

triangles with shared corners. The average $B-O$ distance is $1.36 \text{ \AA}$ and the average $O-O$ distance $2.35 \text{ \AA}$. Sodium has a coordination number of seven with an average $Na-O$ distance of $2.53 \text{ \AA}$.

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